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Influence of Carbon Nano Tubes on the Thermo-Mechanical Properties of Unsaturated Polyester Nanocomposite

A K M Moshiul Alam, M D H Beg, Rosli Mohd Yunus

Faculty of Chemical and natural Resources Engineering, University Malaysia Pahang, 26300, Gambang, Kuantan, Pahang, Malaysia

akmmalam@gmail.com

Abstract. To date nano fillers are renowned reinforcing agent for polymer materials. In this work, unsaturated polyester (UPR) nanocomposites were fabricated by 0.1, 0.3 and 0.5 wt% multi walled carbon nanotubes (MWCNTs) through solution dispersion and casting method. The influence of MWCNT content was investigated by thermo-mechanical properties. Dispersion of nanotubes was observed by fracture morphology. The strength of nanocomposites rose with raising the CNT content. Moreover, DSC thermograms of nanocomposites represent noticeable improvement of glass transition temperature (T_g), melting temperature (T_m) and enthalpy (ΔH_m). Micro-crystallinity of nanocomposites increased with increasing the CNT content. Moreover, the stiffness increased with increasing the CNT content.

Key word: Solvent dispersion, Nanocomposites, Characterization

1. Introduction

The unsaturated polyester resins (UPRs) are common thermosetting resins and steadily increasing their applications for several purposes because of their sound properties, cost effectiveness as well as simple handling. However, cross-linked UPRs have limited structural reliability, therefore, before cross-linking they are often mixed with reinforcing materials such as natural fibers, synthetic fibers, nanofillers as well as mineral fillers and so on [1,2,3,4]. The reinforced composites are devoted for construction, marine and automotive industries due to their light weight and durability.

The carbon nanotubes (CNTs) are more attractive fillers in the vicinity of polymer composites because of their outstanding properties therefore they are substitute of conventional macro and micro fillers [5,6,7]. CNTs are geometrically distinctive to their surface area, provide an immense resources of interaction with any continuous phase giving rise to great opportunity for effective load transfer [8]. Moreover, small amount of CNT with efficient dispersion in matrix exhibit considerable enhancement of different properties [9]. The significant improvement of properties are determined by the degree of CNTs dispersion and interfacial adhesion into the composite system [10]. Conversely, several phenomena restrict carbon nanotube dispersions, such as nanotube morphology and Van der Waal's forces between nanotube surfaces. Not only that but also the high aspect ratios together with the high flexibilities noticeably increase the possibilities for entanglements. These entangled aggregates are very complicated to separate into individual nanotubes [11]. The interaction of CNTs reveal high potential energy which naturally making them more difficult to separate as individuals nanotubes [12,13]. Therefore, different physical and chemical methods are demonstrated for control dispersion of individual nano tubes in matrix. Physical methods consider for direct mixing through mechanical force. Chemical methods are carried out by surfactants action, functionalization of carbon nanotube, surface modification, and polymer wrapping technology [14,15]. For instance, studies related to thermoset nanocomposite systems have shown that share mixing strategies for dispersion of CNT. It has carried out at room temperature with different non hydrogen bonding Lewis base solvents to take away the nanotube surface interaction [16,17,18].

Corresponding author: Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Gambang 26300, Kuantan, Malaysia. akmmalam@gmail.com (A.K.M.Moshiul Alam)



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Moreover, UPR has huge market compare to other resins, there have only been limited investigations of MWCNT dispersions in UPR [19,20]. Apparently, the small number of efforts has been paid to disperse MWCNTs in UPR and characterization of thermo-mechanical properties. Consequently, first of all we have emphasis on the dispersion of MWCNTs in UPR matrix in association of solution and sonication techniques. We report the effect of CNT content in UPR, as well as focus on the interaction between matrix and MWCNTs in the nanocomposite networking system. Furthermore, compare the properties of neat resin and nanocomposites for determining efficiency of MWCNT.

2. Materials and methods

2.1 Materials

The orthophthalic unsaturated polyester resin (Polymal) was used as received from Luxchem Polymer Industries *Sdn. Bhd.*, Malaysia. The viscosity of resin is 700-800mPa.s at 25°C. volatile content 30-35%, Gel time 8-15min. Multi Wall Carbon Nanotubes (MWCNT) produced by moving-bed catalysis technique, diameter <8nm, length between 10 - 30 μm , and the carbon purity 95% received from Timesnano, China. Tetra-hydro Furan (THF), received from Merk, Germany. Methyl Ethyl keton peroxide (MEKP) purchased from Sigma Aldrich, USA.

2.2 Composite fabrication

First of all, 0.1, 0.3 and 0.5 wt% MWCNT mixed separately with THF solvent, the MWCNT: THF ratio was maintained as 1:25. The suspension stirred by magnetic stirrer for 15 minutes followed by sonication in ultra sound bath for 1hour. After that, it mixed with resin and stirred again for 15 minutes, subsequently sonicated for 2 hours. Secondly the resin/CNT suspension heated at the boiling temperature of THF (66°C) for 5 minutes to evaporate the solvent. The warm suspension placed in a cold water bath to cool at room temperature. 1 wt% MEKP added in this suspension and gently stirred for 3 minutes, then placed in vacuum to remove the bubbles. Finally, the bubble free mixture poured on the specimen mold and cured at room temperature. In this manner, the samples prepared for subsequent analysis were neat unsaturated polyester resin (UPR), 0.1wt% MWCNT reinforced UPR nanocomposite (0.1MWCNT- UPR), 0.3wt% MWCNT reinforced UPR nanocomposite (0.3MWCNT- UPR) and 0.5wt% MWCNT reinforced UPR nanocomposite (0.5MWCNT- UPR).

2.3 Field emission scanning electron microscopy (FESEM)

Composites fracture surfaces investigated by using a (JOEL, JSM-7800F, Japan) field emission scanning electron microscope. Samples mounted on aluminium stubs with carbon tape followed by sputter coated with platinum to make them conductive prior to FESEM observation.

2.4 Tensile testing of composites

Tensile testing was conducted according to ASTM 638-08, using a Shimadzu (Model: AG-1) Universal tensile testing machine fitted with a 5 kN load cell operated at a cross-head speed of 1mm/min and keeping 65 mm gauge length. Tensile strength (TS), tensile modulus (TM) and elongation at break (EB) are obtained by this testing method. Five samples of each category were tested for analysis the data.

2.5 Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed to determine transition states of material, for instance, the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m), using a TA/Q1000 apparatus under nitrogen atmosphere. During DSC analysis, the samples were initially heated at 30 – 400°C with a heating rate 10°C min⁻¹ in nitrogen atmosphere.

3. Result and discussion

3.1 Mechanical properties

Figure 1 represents the (a) TS and TM and (b) EB of nanocomposites as a function of MWCNTs content. The results represent those MWCNTs able to improve the mechanical properties of UPR. Furthermore, 0.1, 0.3 and 0.5 wt% MWCNTs loaded MWCNT-UPR nanocomposites exhibited enhancement of TS, TM. The increased TS of 0.1MWCNT-UPR, 0.3MWCNT-UPR and 0.5MWCNT-

UPR nanocomposites are 10%, 29% and 21% correspondingly, similarly the TM rose of 51%, 88%, and 80% respectively and the EB% decreased as well.

It is obvious, that the 0.3MWCNT-UPR exhibits better mechanical performance than 0.1MWCNT-UPR and 0.5MWCNT-UPR. When the CNT content increased more than 0.3 wt% MWCNT undergo partial agglomeration represents in FESEM micrograph, which limits the efficiency of reinforcement. Such a phenomenon also observed in other reports [21,22]. It is true that, individual nano tubes enjoy both large surface area and strong interfacial interactions with matrix these inherent advantages lead to efficient stress transfer between the MWCNTs and the UPR, and avoid the deformation or fracture of the composites under external force [21]. In addition, the lowest elongation of 0.3MWCNT-UPR nanocomposite credibly MWCNTs are complimentary of the non elastic deformation.

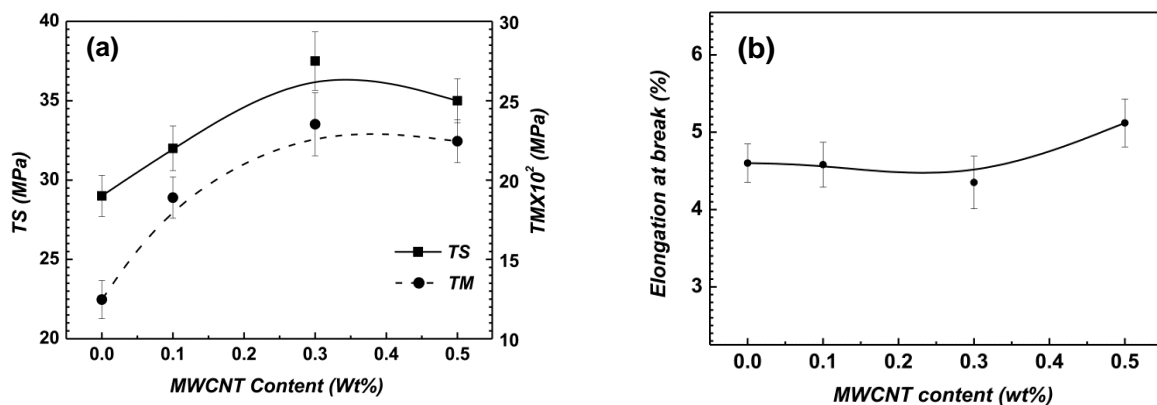


Figure 1. (a) Tensile strength and tensile modulus (b) Elongation at break of nanocomposites as a function of MWCNT content

3.2 Fracture Morphology

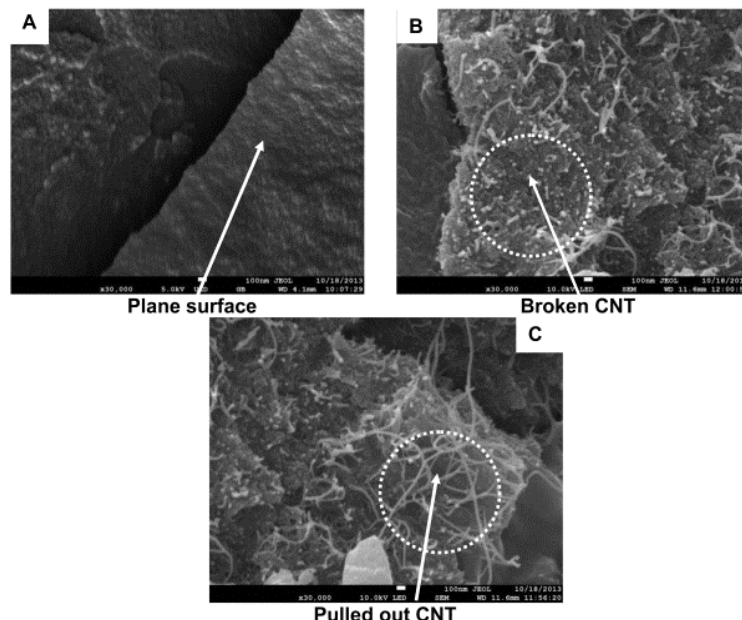


Figure 2. Fracture morphology of (a) UPR, (b) 0.3MWCNT-UPR and (c) 0.5MWCNT-UPR. Figure 2 illustrates the fracture morphology of (a) UPR, (b) 0.3MWCNT-UPR and (c) 0.5MWCNT-UPR nanocomposites. The surface of neat resin in figure 2(a) is smooth and distinctly cracking whereas nanocomposites surfaces are rough and CNTs tend to bridge the cracking. Several bright fractured tips of nanotubes represent by dotted circle remained in the matrix and they were not pulled

out during stretching of 0.3MWCNT-UPR nanocomposite shown in figure2b. In this case, matrix tends to stick to the CNTs by well wetting and Van der Waals force, as a result, increased the composite TS and TM. Furthermore, the nanotubes tend to nucleate cracking and propagate the rough surface of nanocomposites which implies that the CNT–UPR interface is strong as well as providing for an additional reinforcement effect thus more energy is needed to break the specimens. On the other hand, in case of 0.5MWCNT-UPR nanocomposite in figure 2(c) CNT pull out region evidently mentioned by dotted circle. This is because high concentration of CNT formed agglomeration, thus declined the resultant composite's reinforcement.

3.3 DSC Analysis

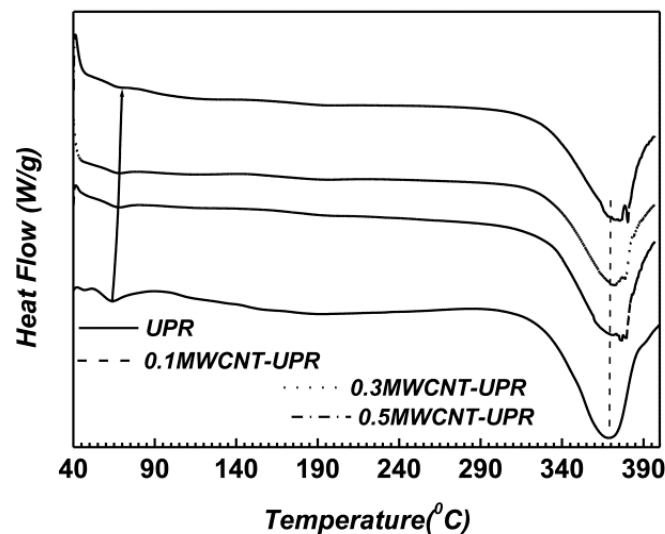


Figure 3. DSC thermogram of (i) neat UPR, (ii) 0.1MWCNT-UPR, (iii) 0.3MWCNT-UPR and (iv) 0.5MWCNT-UPR

Figure 3 illustrates the DSC thermograms of (i) neat UPR, (ii) 0.1MWCNT-UPR, (iii) 0.3MWCNT-UPR and (iv) 0.5 MWCNT-UPR nanocomposites. They notice the information of chain intercalation and thermal transitions of nanocomposites. The endotherm in the lower temperature region around 60-67°C ascribe to the glass transition (T_g). Furthermore, the endothermic transition around 366-382°C are related to the melting temperature(T_m).

Table1. The T_g , T_m and ΔH_m values obtained from DSC thermograms.

Samples	T_g °C	T_m °C		ΔH_m Jg ⁻¹
		T_{m1} °C	T_{m2} °C	
UPR	64	369	-----	0.56
0.1MWCNT-UPR	67	371	376	0.64
0.3MWCNT-UPR	67	371	382	0.81
0.5MWCNT-UPR	65	371	382	0.61

The nanocomposites exhibit a split melting endotherm into two peaks (T_{m1} and T_{m2}), instead of one endothermic peak as shown by pure matrix. The presence of double-melting peaks for the nanocomposites may indicate the bond formation between MWCNT and UPR. The melting peak at T_{m2} is a precursor to identify the binding energy among nanotubes and UPR molecules. The T_g , T_m and ΔH_m values of these samples represent in table 1.

MWCNT content significantly influenced the glass transition temperature of nanocomposites, which can be explained by the formation of microcrystalline segments, they are relatively well-ordered as well as enhance the degree of curing, moreover which restrict the resin chain mobility in the surrounding area of CNT [23,24,25]. Taking into account, amorphousness of UPR matrix, some nucleating effect provided by MWCNTs is to be assumed. In fact, DSC thermogram of neat UPR confirms the amorphous behaviour. In presence of MWCNT nanofillers, nucleation of micro crystallization takes place in the host matrix. In case of nanocomposites the apparent crystallization takes place thus the corresponding melting enthalpies are higher than neat matrix. The greater degree of micro crystallinity in 0.3MWCNT-UPR composite is reflected in the higher enthalpy value. It is also interesting that the heat of transition increased significantly in case of composite specimens. It is obvious that MWCNT acting as a key nucleating agent.

4. Conclusion

0.3MWCNT-UPR shows the highest mechanical properties compared to neat UPR and other nanocomposites. These results indicate a considerable enhancement of materials properties by the incorporation of MWCNT in matrix. The fracture morphology confirmed 0.3 wt% MWCNT is preferable for well dispersion and interaction between UPR and MWCNT. The glass transition temperature and melting temperature and micro crystallinity were noticeably increased in nanocomposites.

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